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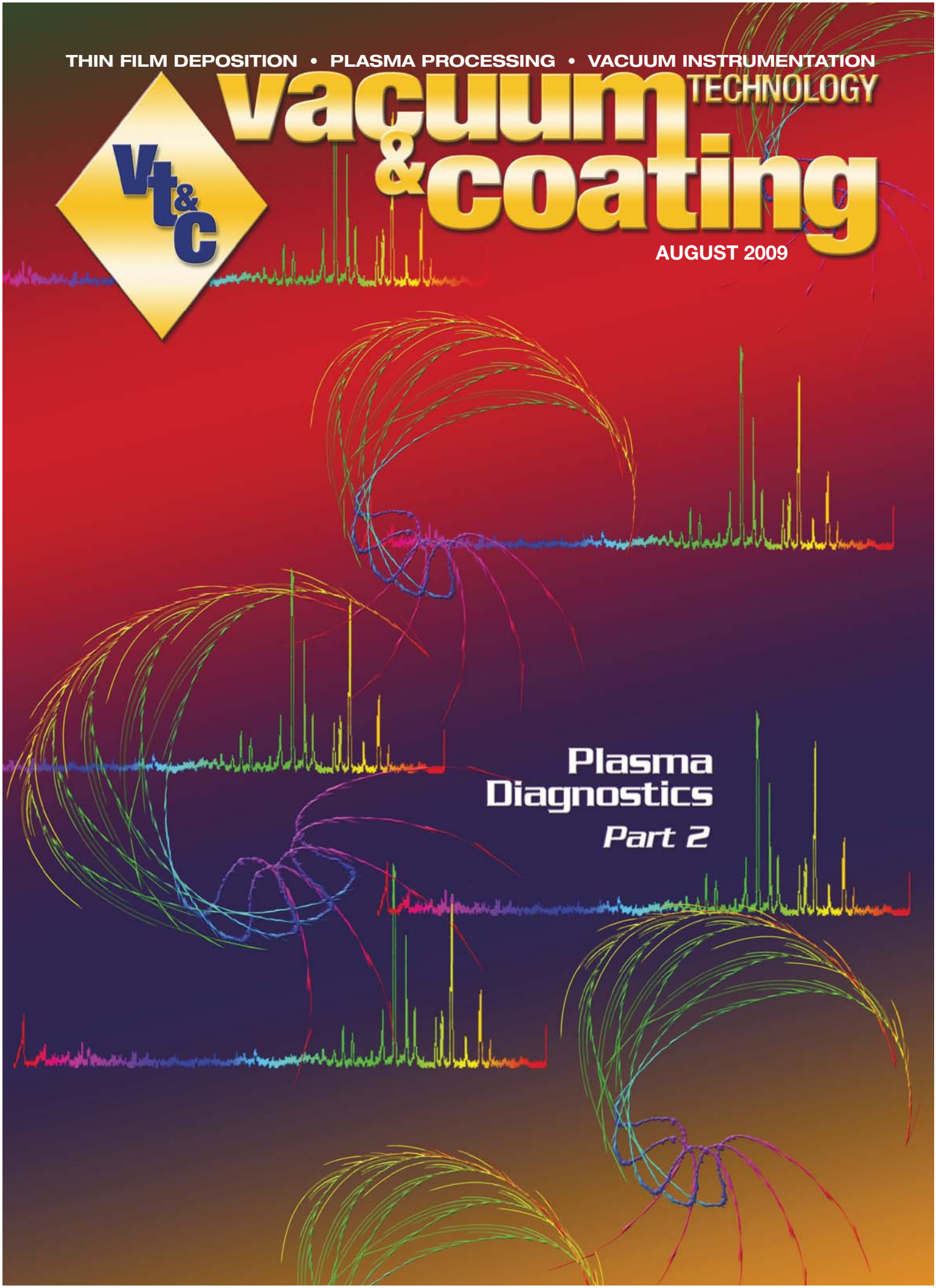
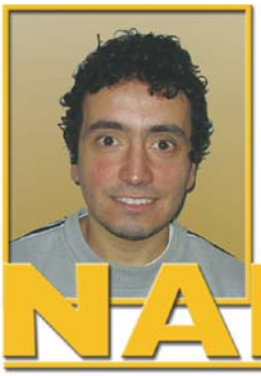


Plasma Diagnostics

Part 2



NANOtechnology

Plasma-Nanoscience: Plasma-Aided Advanced Nanofabrication Tools for Functional Nanomaterials and Devices

By Evgeniya H. Lock, Scott G. Walton, Ilker S. Bayer, Abhijit Biswas *Contributing Editors*

Plasma-nanoscience involves plasma-aided nanofabrication of functionalized new nanomaterials, exotic nanostructures and advanced nanodevices [1]. It is an emerging interdisciplinary research area that covers plasma science, materials science, applied physics, applied chemistry, electronics, nanoscience and nanotechnology, electrical, mechanical, biological and process engineering. Plasma-based processing provides control over the generation, transport, deposition, and incorporation of the building units of nanomaterials and structures that are otherwise difficult to achieve by existing nanofabrication techniques. As demonstrated in many industries – the semiconductor industry is one example – plasmas processing can be used to rapidly and uniformly treat large surface areas, which is paramount to successfully industrializing any technology.

Plasma, the fourth state of matter, is defined as a collection of freely moving charged particles (electrons and ions), radicals (neutral molecular fragments), as well as long- and short-lived excited species (the latter typically produces, via photon emission, the characteristic glow of a plasma). An intrinsic property of the plasma is to preserve its overall charge neutrality, meaning equal numbers of positive and negative charges exist. At the plasma-surface interface however, this neutrality breaks down across a region called a sheath, where charge seperation produces strong electric fields, which accelerate ions toward the surface. The delivery of high energy ions to adjacent surfaces marks one of unique attribute of plasmas.

Although plasma devices vary widely in their design, they are commonly produced by applying an electric field, either AC or DC, to a volume of gas. Most of the energy is transferred to the electrons so that a small fraction is energetic enough to ionize the background gas, thereby sustaining the plasma. Depending on the temperatures of the electrons, ions and neutrals, plasmas can be classified as equlibrium (thermal) and non-equilibrium (non-thermal) plasmas. In the equilibrium plasmas, $T_e \sim T_i \sim T_n$ where subscripts e, i and n denote electrons, ions and neutrals respectively. This means that the average kinetic energy of all species is approximately the same (typically 1.5 eV, 1 eV ≅ 11 600 K). In these plasmas there is a high degree of ionization, in many cases approaching full ionization. In non-equlibrium plasmas there is a significant kinetic energy difference between the constituent particles. Most neutral and ionic species are near room temperature, while most of the electrons are in the range of 1-10 eV, depending on the plasma processing device [2]. It is these high energy electrons which are largely responsible for the uniques gas-phase chemistries available in plasmas. Indeed, one of the reasons that plasmas have assumed a dominant role in materials processing is their ability to produce a broad range of inert and reactive species (gas dependent), deliver them to a surface and thus change the material's physical and chemical properties. This, along with the delivery of energetic ions at plasma-exposed surfaces, allows for better control of the self-organization of nanostructure building blocks and their precise insertion into the nanoassemblies [1,3]. It is for these reasons that plasma-aided nanofabrication tools are considered superior compared with neutral gas-based (e.g. chemical vapor deposition (CVD), molecular beam epitaxy (MBE), cluster beam deposition, etc.)

and other (e.g. wet chemical, electron beam, microlithography, flame) fabrication routes [1].

Before discussing a a select few examples of plasma applications, it is useful to define the terms *nanostructure, nanoassembly* and *nanofabrication*. A *nanostructure* has dimensions ranging from one to tens of nanometers (1nm =10^{-9} m). A few examples include quantum dots, carbon nanotubes, and metallic nanoparticles. A *nanoassembly* is the association of atoms in the size range of one to tens of nanometers, e.g. nanoclusters, nanocrystals, nanostructured films, nanopatterns, and arrays. *Nanofabrication* is a production of functionalities, elements, materials and ultimately coatings and devices that contain nanoscale features or have been made by using nanostructures or nanoassemblies as building blocks [4]. Examples of nanofabrication include biosensors for protein recognition and plasma assisted anotransfer printing.

First, let us focus our attention on plasma generated nanostructures and nanoassemblies. Nanostructured materials are expected to lead the major advances in electronics and photonics in the next decades. In nanometer-sized semiconductors and metals the valence and conduction bands may split into discrete electronics levels whose spacing increases with decrease of particle size [5]. Quantized matter can adopt different shapes (dots, wires, etc.) depending on quantization dimensions [6]. Low-pressure, plasma-enhanced chemical vapor deposition (PECVD) techniques have been used for thin film deposition and surface treatment since the early 1960s [7,8] and have been extensively used in the microelectronics industry. **Figure 1** illustrates the growth and crystallization of quantum dots (QD) on a plasma-exposed surface. This includes the most important processes involved in the growth: the incoming flux of ionic species (green) and the migration of adsorbed species (shown as blue spheres) in the areas between the nanocrystals (shown as ordered cubic stacks of golden spheres) and over the surfaces of different crystalline facets of the nanoparticles (red spheres) [3].

Charged carbon clusters in the nanometer scale can be used for synthesis of single-crystalline diamond or of crystalline graphite [4]. Researchers have also used plasmas to control the amount of oxygen in graphene-oxide [9,10]. Reducing the amount of oxygen has been shown to increase the conductivity of the material and the process requires seconds compared to several hours using chemical approaches [9]. It is interesting to note that reduced graphene-oxide begins to approximate the electrical characteristics of graphene, a single monolayer sheet of sp^2-bonded carbon, but is more chemically reactive.

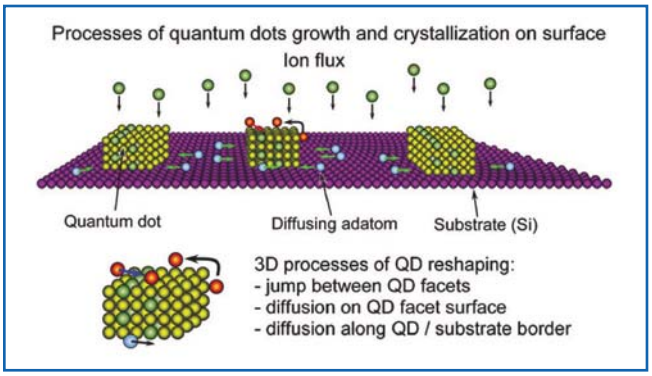

Processes of quantum dots growth and crystallization on surface
Ion flux
Quantum dot
Diffusing adatom
Substrate (Si)
3D processes of QD reshaping:
- jump between QD facets
- diffusion on QD facet surface
- diffusion along QD / substrate border

Figure 1. Schematic illustration of nanoparticle growth and crystallization on a plasma-exposed surface. Reproduced from [3].

Since the discovery of carbon nanotubes by S Iijima in carbon soot generated in thermal arc discharge plasma [11], PECVD technology has been extensively used to fabricate particularly carbon nanomaterials. Advantages of this technique include (1) the ability to synthesize carbon nanostructures on temperature sensitive substrates, (2) an anisotropic flux of energetic ions across the plasma sheath appears to be the main factor for carbon nanostructure alignment, which is not achievable by non-plasma based methods, and (3) by varying the gas and power deposition, one can achieve control over the competing growth and etching processes and thus control the shape of the carbon nanostructures [12].

A few examples of plasma produced carbon nanotubes include freestanding individual, pristine single-walled carbon nanotubes (SWNTs), junction structure encapsulated SWNTs, and DNA encapsulated SWNTs, alkali-metal/fullerene etc. with new functions by using various kinds of plasma sources such as pair-ion plasma, alkali-fullerene plasma, alkali-halogen plasma, micro electrolyte plasma, solution-phase discharge plasma etc. [13]. Plasmas have also been used to selectively remove metallic nanotubes from semiconducting ones in an effort to produce high current transistors [14]. Further, carbon nano-necklaces were produced by plasma-aided deposition (**Figure 2**) [15]. The

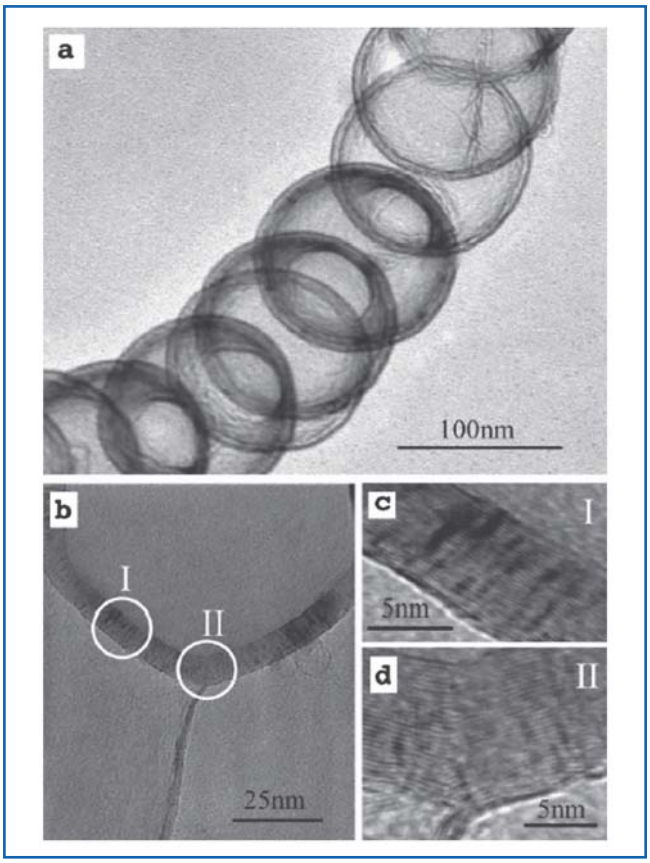


Figure 2. Ttransmission electron microscope images of a carbon nano-necklace showing (**a**) the connection between elementary units (nano-bells), (**b**) detail showing the graphene-based shells that make up a nano-bell and (**c**) and (**d**) show details of the regions I and II shown in (**b**). Reproduced from [15].

researchers attributed the growth of the nano-necklaces to the presence of liquid catalytic particles, which requires high temperatures (2000– 2700 K), such as only readily attainable using thermal plasma processes [15].

Recent developments in plasma-aided nanofabrication have produced controlled pathways for successful fabrication of various semiconducting inorganic nanomaterials, which hold outstanding promise for advanced optoelectronic, nanoelectronic, bionanosensor, and next generation photovoltaic applications [4, 16-19]. For practical applications, the important considerations, among others, are the perfect crystalline structure; homogeneity of the main attributes of individiual nanostructures (size, structure, crystallinity, composition etc.) and the desired shape (e.g. aspect ratio, facets etc.) within the size range, which is usually below the exciton' Bohr radius (~1-10 nm) [3]. Self assembled size-uniform ZnO nanoparticles, ultra-high-aspect ratio Si nanowires, vertically aligned cadmium sulfide nanostructures, and quarternary semiconducting SiCAIN nanomaterial have been successfully synthesized using a low-temperature plasma-enhanced physical vapor deposition (PEPVD) [3, 20-22]. **Figure 3** shows electron microscope images of plasma-synthesized ZnO nanoparticles (**a**), high-aspect ratio Si nanowires (**b**) and vertically aligned CdS nanostructures (**c**). These nanomaterials were synthesized by the inductively couple-assisted RF magnetron sputtering.

In other work, plasma-aided nanofabrication was used to synthesize silicon nanograss and Ge nanocones and porous films

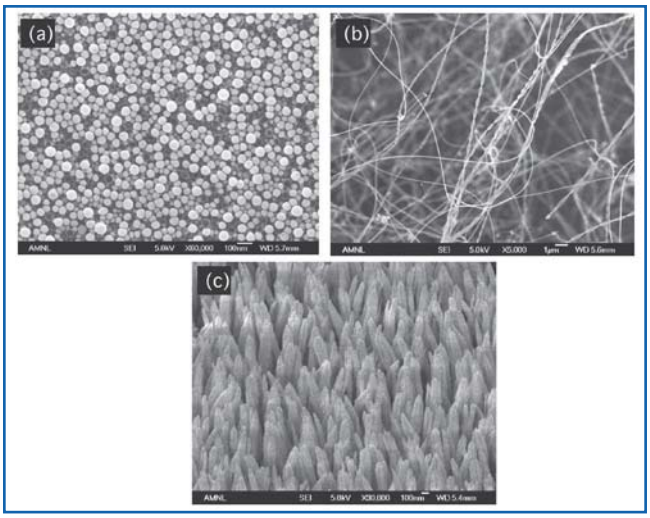
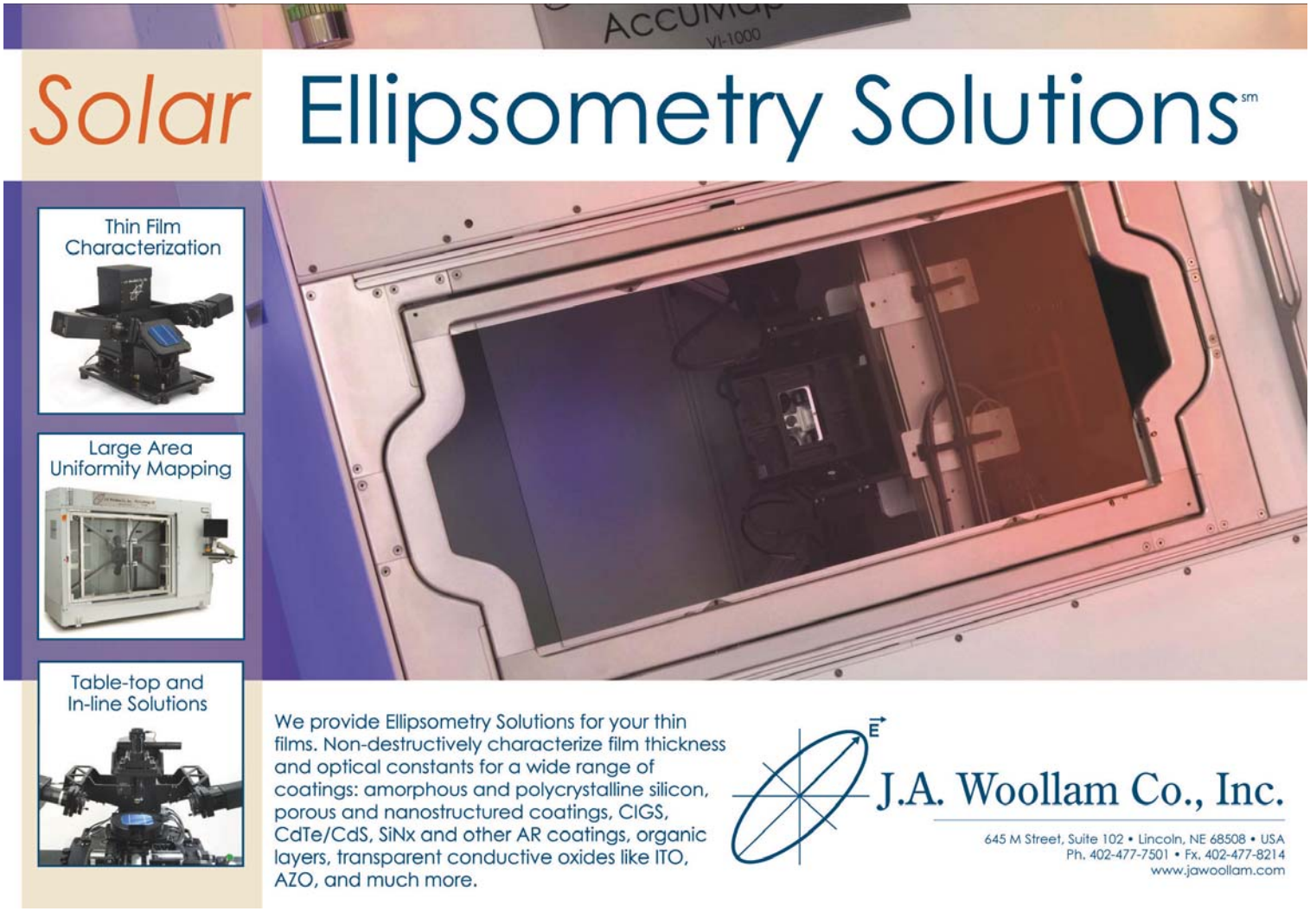


Figure 3. SEM images of plasma-aided nanofabrication of different nanomaterials: (**a**) ZnO nanoparticles on nanocrystalline silicon buffer interlayers (**b**) ultra-high-aspect-ratio silicon Nanowires (**c**) vertically aligned CdS nanostructures. Reproduced from [3].

[23]. Hydrogen plasma etching was employed to etch the Si surface to create nanostructures for antireflective properties. **Figure 4** shows SEM images of the Si nanograss samples etched for different times. The researchers found that when silicon is exposed to inductively coupled hydrogen plasma alone, a uniform nanograss with a diameter of about 20 nm can be created by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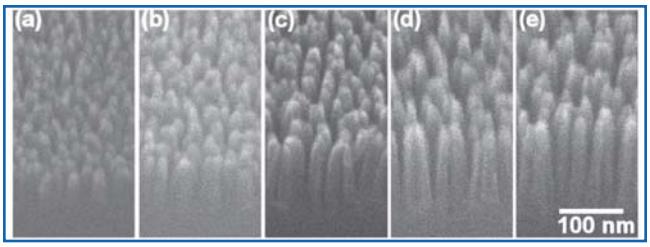

Figure 4. SEM side-view images of Si nanograss etched for (**a**) 10, (**b**) 20, (**c**) 30, (**d**) 40 and (**e**) 50 min. Reproduced from [23].

dual-frequency plasma due to the increase in the ion energy across the sheath. The results showed that the physical bombardment determines the etching rate of Si when exposed to hydrogen plasma. The resulting antireflective properties of Si nanograss showed reduction in the reflectance below 4.5% in the range DUV to near-IR (200–900 nm) as the wafer was etched for 40 min [23].

Nanofabrication of a new class of flexible electronics devices and biosensors include surface/interface nanotexturing and precise control over the final nanoassembly composition and structure. There are three main routes to achieve nanotextured material including etching/sputtering, nanostructures deposition and patterning [12]. The precise control over the deposited nanoassembly includes phase control, elemental composition, doping, functionalization, multilayers and post-processing. As a result, a nanoassembly with desired functionality can be incorporated in a biosensor [24,25] or be a critical step in nanoprinting process for flexible electronics applications [26].

Figure 5 shows a protocol for template imprinting of proteins, in which plasma deposited film plays a key role. First, a template protein is absorbed onto a freshly cleaved mica in citrated phosphate-buffered saline (SPBS). Then a 1-10 mM solution of disaccharide is spin cast to form 10-50 A° sugar overlay. The sample is then exposed to a RF-generated (13.56 MHz) plasma and a 10-30 nm fluoropolymer thin film C_3F_6 is deposited. The resulting plasma film is fixed to a glass coverslip using epoxy resin and oven-cured. Mica is then peeled off and the sample is soaked in a NaOH/NaClO (0.5/1%) solution for 0.5-2 hr for dissolution and extraction of protein. A nanopit with a shape complementary to the protein is created on the imprint surface. The researchers propose that these nanopits/nanocavities can specif- ically recognize their template proteins [25].

In conclusion, the field of plasma-aided nanofabrication is rapidly expanding and presents unique opportunities to scientists and engineers not only for fundamental research in understanding mechanisms of nanostructure formation but also for applied research in developing novel materials and processes for practical applications. The important advantages of plasmas lie largely in the unique species generated in the bulk plasma, and their delivery, along with a flux of energetic ions to the surface of the material. This provides a certain flexibility so that plasmas can be used to etch features with nanoscale dimensions, introduce nano-scale functionalities, and conformally coat nanoscale features. These unique attributes, coupled with the fact that plasmas can rapidly and uniformly treat large area, make plasma an

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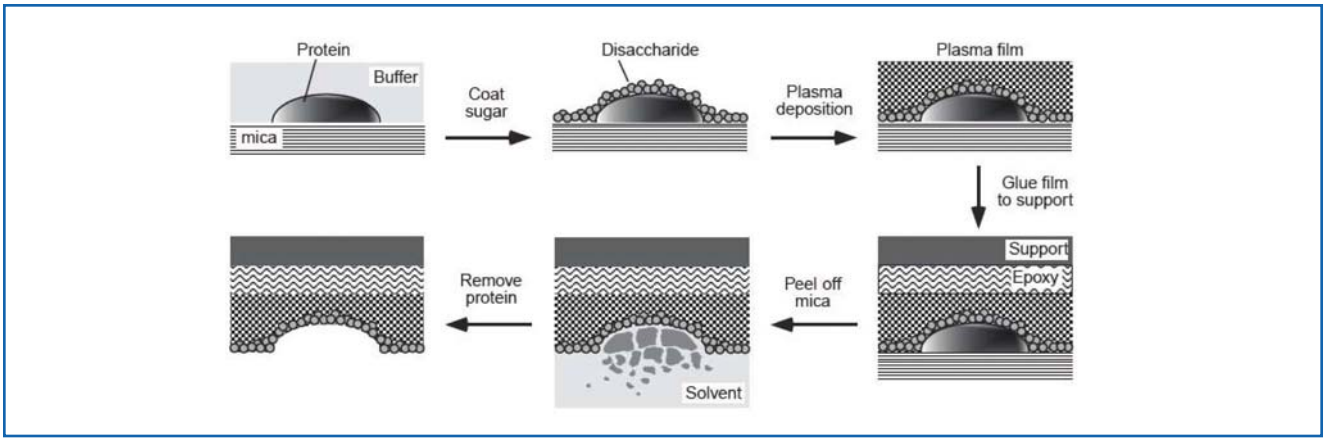

Figure 5. Protocol for template imprinting of proteins. Reproduced from [25].

ideal tool to bring nanofabrication to maturity. As such, it is anticipated that plasma will play significant role in the near future in the fabrication of industrially applicable novel nanomaterials and nanodevices.

About the Guest Contributing Editors

Evgeniya H. Lock, PhD, is completing her postdoctoral work as a National Research Council Fellow at the Plasma Physics Division of the Naval Research Laboratory in Washington, DC. She obtained her Ph.D. in mechanical engineering in 2006 from the University of Illinois at Chicago, during which she received the Air Liquide Fellowship (2004). E. H. Lock received her M.S. in chemical process engineering in 2002 from the University of Chemical Technology and Metallurgy (UCTM) in Sofia, Bulgaria, during which she received Diploma Research Scholarship for her thesis work at the Technical University Hamburg-Harburg in Hamburg, Germany. She also worked at Bayer AG in Leverkusen, Germany.

Scott G. Walton, PhD, is a staff scientist at the Plasma Physics Division of the Naval Research Laboratory. Prior to joining the laboratory staff, he was a National Research Council postdoctoral research associate at the laboratory. Dr. Walton is the principal investigator (PI), Co-PI, and manager of several programs involving plasma generation and plasma-based materials processing. He has over 50 papers on ion-surface interactions, plasma diagnostics, electron beam generation, and plasma processing; he has written two book chapters on plasmas for processing; he has 1 US patent, 5 patent applications, and 2 statutory invention registrations.

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